Thermodynamics of Aluminum, Nitrogen and AlN formation in Liquid Iron

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Thermodynamics of aluminum, nitrogen and AlN formation in liquid iron was investigated using the metal–nitride-gas equilibration under various nitrogen partial pressures in the temperature range of 1873–1973 K. The nitrogen solubility in liquid iron decreased with aluminum additions. Pure solid AlN was formed at critical contents of aluminum and nitrogen in liquid iron. The experimental results were thermodynamically analyzed using Wagner’s interaction parameter formalism to determine the first-order interaction parameter of aluminum and nitrogen, the first-order self interaction parameter of aluminum, and the equilibrium constant for the formation of pure solid AlN in liquid iron as follows.

\[
\begin{align*}
\varepsilon_{\text{N}}^{\text{Al}} &= -332.2/T + 0.194 \\
\varepsilon_{\text{Al}}^{\text{Al}} &= 111.0/T - 0.016 \\
\text{AlN (s)} &= \text{Al} + \text{N} \\
\log K_{\text{AlN}} &= -16.660/T + 7.4
\end{align*}
\]

Thermodynamics of aluminum in liquid iron could be well described by Darken’s quadratic formalism, and the values of \( \alpha_{\text{Fe-Al}} \) and \( \gamma_{\text{Al}}^{o} \) were determined as follows.

\[
\begin{align*}
\alpha_{\text{Fe-Al}} &= -1.112/T - 0.585 \\
\gamma_{\text{Al}}^{o} &= -185.0/T + 0.165
\end{align*}
\]

KEY WORDS: liquid iron; aluminum; nitrogen; AlN; equilibrium constant; interaction parameters.

1. Introduction

Aluminum is one of the most important alloying elements used for deoxidizing liquid steels. Recently, thermodynamics of Fe–Al–N system and the reaction equilibrium of AlN formation in liquid steel became also important for some special grades of steels containing high aluminum contents of greater than 1 mass%. In spite of such importance, there is huge scatter in interaction parameter values between aluminum and nitrogen and the equilibrium constant of AlN formation reaction in liquid iron in the literature including the recommended values of the Japanese Society for the Promotion of Science (JSPS).1) For an example, the effect of aluminum on the activity coefficient of nitrogen in liquid iron, \( \varepsilon_{\text{N}}^{\text{Al}} \) measured by several investigators are positive \(^{2-4}\) and others are negative \(^{5,6}\) as shown in Fig. 1. Furthermore, the recommended values in JSPS for \( \varepsilon_{\text{N}}^{\text{Al}} \), \( \varepsilon_{\text{Al}}^{\text{Al}} \) and the equilibrium constant, \( K_{\text{AlN}} \) for the formation of AlN in liquid iron were taken from different sources \(^{2-8}\) where the data were determined by completely different experimental techniques. This will cause significant errors in predicting the reaction equilibrium in Fe–Al–N system.

![Fig. 1. Relations between log(\(f_N^o\)) and [%Al] reported by various authors at 1873 K.](image-url)
In the present study, thermodynamics of aluminum, nitrogen and AlN formation in liquid iron was investigated using the metal–nitride-gas equilibration technique in the temperature range of 1 873–1 973 K. The sampling method utilizing a high frequency induction furnace was used to determine the equilibrium relations of aluminum and nitrogen in iron melts containing up to 4.53 mass% Al at different nitrogen partial pressures. The effect of aluminum content on nitrogen solubility in liquid iron was measured. The solubility product of aluminum and nitrogen in liquid iron saturated with pure solid AlN was also measured as a function of temperature. Using Wagner’s formalism, the interaction parameters of aluminum and nitrogen and the equilibrium constant of AlN formation in liquid iron were determined and compared with previous investigations. In addition, thermodynamics of aluminum in liquid iron determined in the present study were examined by Darken’s quadratic formalism.

2. Experimental Procedures

Five hundred grams of high purity electrolytic iron (99.95 mass% purity, 200 mass ppm O, <5 mass ppm N, 18 mass ppm C, <10 mass ppm Si), contained in an Al₂O₃ crucible (OD: 56 mm, ID: 50 mm, H: 96 mm) was melted in the temperature range of 1 873–1 973 K by a 15 kW/30 kHz high frequency induction furnace as shown in Fig. 2. The alumina crucible was placed in a graphite crucible and a porous alumina crucible as outer crucibles. The reaction chamber consisted of a 96 mm OD quartz tube open at both ends and was connected to a gas delivery system.

After melting the iron, the temperature of the melt was monitored by a Pt/Pt–13 mass%Rh thermocouple sheathed with an 8 mm OD alumina tube immersed in the melt. Any possible influence of high frequency noise on the temperature reading was avoided by grounding the circuit of the thermocouple. Preliminary trials confirmed that no significant noise was detected. The temperature fluctuation of iron melt could be controlled within 2 K during experiment by the PID controller of the induction furnace. The temperature reading of the PID controller was calibrated by the sourcing DC voltage calibrator for the thermal EMF of R-type thermocouple.

After the temperature of melt was reached to a desired value, an Ar–10%H₂ gas was blown onto the melt surface at a high flow rate of ~5 000 mL/min for 2 h to deoxidize the iron melt. The oxygen content in the melt after this procedure was in the range of 15–20 mass ppm. Then the gas was switched to a N₂–3%H₂ gas (P(N₂) = 0.97 atm) or a mixture of Ar–10%H₂ and N₂ gases (P(N₂) = 0.2 atm). The flow rate of gas mixture was controlled by a mass flow controller in the range of 1 000 to 2 000 mL/min depending on nitrogen partial pressures in the gas.

Strong agitation of melt by an induction furnace resulted in a fast attainment of equilibrium nitrogen solubility in liquid iron under a nitrogen partial pressure within 1 h. After confirming the saturation of nitrogen in liquid iron at a nitrogen partial pressure by sampling and analysis of the melt with time, aluminum pellets (99.9 mass% purity) were dropped into liquid iron through a 20 mm OD quartz tube. After the predetermined equilibrium time of 1 h, a metal sample of about 10 g was extracted by a 6 mm OD quartz tube connected to a syringe (10 mL), and it was quenched rapidly in water within 2 s. Aluminum addition and sampling were repeated until a stable AlN layer was formed on the surface of the iron melt.

The metal samples were carefully cut for the chemical analysis. Four specimen of each metal sample were prepared for the analysis of nitrogen and oxygen. The nitrogen and oxygen contents in the metal sample were measured with the inert gas fusion-infrared absorptiometry technique with an accuracy of ±1 mass ppm. For the analysis of aluminum and silicon, the metal sample (0.2 g) was dissolved in 20 mL of HCl(1+1) in a glass beaker of 50 mL capacity heated in a water bath for 2 h. The leaching test of AlN powder (98% purity, <10μm) in various acid solutions indicated that AlN was nearly insoluble in dilute HCl(1+1) solution heated in a water bath up to 6 h. After dissolving the sample, the solution was transferred to the measuring flask (100 mL) with filtration. Aluminum and silicon dissolved in sample solution were then analyzed by the ICP-AES using appropriate standard solutions containing the same amount of Fe (2 000 mass ppm) as sample solutions. The analytical limits of aluminum and silicon in metal sample were 5 ± 1 mass ppm and 1 ± 0.2 mass ppm, respectively.

After each experimental run, the Fe–Al–N melt contained in an alumina crucible was quenched rapidly by helium gas blowing onto the melt. The quenched metal sample was cross-sectioned and examined with an optical microscope for the presence of AlN inclusions. The center part of metal sample was virtually clean without any noticeable AlN inclusions. However, a few AlN inclusions were observed near the melt surface. Figure 3 shows the results of SEM-EDS analysis on AlN inclusions of ~20μm in size formed in the Fe–Al–N melt.

3. Results and Discussion

One of the main concerns in the measurement of equilibrium nitrogen solubility with aluminum content in the melt by the sampling method was how to retain the dissolved nitrogen and aluminum in metals during sampling. As shown
in Table 1, a separate test was conducted at 1 973 K to see if any delay in quenching would result in a substantial error in determining soluble nitrogen and aluminum contents by the secondary precipitation of AlN. The result showed that quenching the samples in water within 3 s did not invalidate the results. The other experimental concern was the reaction of aluminum in the sample melt with the quartz tube during sampling. Top and bottom parts of extracted and quenched metal samples were analyzed for any silicon pickup by the reduction of quartz by aluminum in the sample melt. Silicon contents in all metal samples were less than 10 mass ppm, and aluminum and nitrogen contents in top and bottom parts of metal samples were nearly the same as shown in Table 2.

### 3.1. Effect of Aluminum on Nitrogen Solubility

The experimental results of nitrogen solubility measurement with aluminum additions in liquid iron under different nitrogen partial pressures are summarized in Table 2. Figure 4 shows the variation of equilibrium nitrogen solubility in Fe–Al–N melt with aluminum additions under different nitrogen partial pressures of 0.2 and 0.97 atm at 1 873,

### Table 1. Variation of dissolved Al and N in metal samples with delayed quenching.

<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>P_\text{N}_0 (atm)</th>
<th>[%Al]</th>
<th>[%Si]</th>
<th>[%N]</th>
<th>Delayed Time, see</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973</td>
<td>0.97</td>
<td>2.256</td>
<td>0.0013</td>
<td>0.0327</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.256</td>
<td>0.0015</td>
<td>0.0328</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.253</td>
<td>0.0037</td>
<td>0.0316</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.247</td>
<td>0.0071</td>
<td>0.0298</td>
<td>10</td>
</tr>
</tbody>
</table>

### Table 2. The contents of Al, Si and N in analyzed parts of extracted samples.

<table>
<thead>
<tr>
<th>P_\text{N}_0 (atm)</th>
<th>Temp. (°K)</th>
<th>[%Al]</th>
<th>[%Si]</th>
<th>[%N]</th>
<th>Analyzed Part</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1873</td>
<td>1.945</td>
<td>0.0006</td>
<td>0.0145</td>
<td>Top</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.942</td>
<td>0.0006</td>
<td>0.0147</td>
<td>Bottom</td>
</tr>
<tr>
<td></td>
<td>1923</td>
<td>2.365</td>
<td>0.0006</td>
<td>0.0184</td>
<td>Top</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.356</td>
<td>0.0007</td>
<td>0.0186</td>
<td>Bottom</td>
</tr>
<tr>
<td></td>
<td>1973</td>
<td>3.787</td>
<td>0.0006</td>
<td>0.0151</td>
<td>Top</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.785</td>
<td>0.0008</td>
<td>0.0149</td>
<td>Bottom</td>
</tr>
</tbody>
</table>
As shown as open symbols in the figure, the nitrogen solubility decreases linearly as the aluminum content increases in the melt. When the aluminum content exceeds a critical value, the nitrogen solubility sharply decreases as shown as solid symbols in the figure due to the formation of AlN in the melt.

The dissolution of nitrogen before the saturation of AlN in liquid iron alloys can be written as

\[ \frac{1}{2} \mathrm{N}_2 (g) = \mathrm{N} \quad \text{(1)} \]

\[ \Delta G_1^{\circ} = 3.598 + 23.89 \, T \quad \text{J/mol}^{17} \]

\[ K_1 = \frac{f_N \, [\%N]}{P_{\mathrm{N}_2}^{1/2}} \quad \text{(2)} \]

where \( K_1 \) is the equilibrium constant for Reaction (1), \( P_{\mathrm{N}_2} \) is the nitrogen partial pressure and \( f_N \) is the Henrian activity coefficient of nitrogen in 1 mass% standard state in liquid iron.

Using Wagner’s relation,\(^9\) the equilibrium constant \( K_1 \) can be rewritten as the following relation using the first order interaction parameters:

\[ \log K_1 = \log f_N + \log [\%N] - \frac{1}{2} \log P_{\mathrm{N}_2} \]

\[ = e_N^{\text{Al}} [\%\text{Al}] + e_N^{\text{N}} [\%\text{N}] + \log [\%N] - \frac{1}{2} \log P_{\mathrm{N}_2} \]

\[ \text{............................................(3)} \]

where \( e_N^{\text{Al}} \) and \( e_N^{\text{N}} \) are the first-order interaction parameters of aluminum and nitrogen on nitrogen, respectively, and the value of \( e_N^{\text{Al}} \) is known to be 0 in the temperature range of 1873–1973 K.\(^{18}\) As mentioned earlier, the silicon content in metal samples was less than 10 ppm. Also, the oxygen content in the melt was kept very low during the experiments. Therefore, the effects of silicon and oxygen on aluminum and nitrogen were assumed to be negligible.

Therefore, Eq. (3) becomes

\[ \log K_1 = \log f_N + \log [\%N] - \frac{1}{2} \log P_{\mathrm{N}_2} \]

\[ = e_N^{\text{Al}} [\%\text{Al}] + e_N^{\text{N}} [\%\text{N}] + \log [\%N] - \frac{1}{2} \log P_{\mathrm{N}_2} \]

\[ \text{............................................(3)} \]
where \( f_N^{Al} \) is the interaction coefficient of aluminum on nitrogen.

Therefore, the value of \( e_N^{Al} \) in Eq. (4) can be determined from the experimental results of nitrogen solubility in Fe–Al melts as a function of aluminum content before the saturation of AlN. Figure 5 shows the values of \( \log f_N^{Al} \) plotted vs. percent aluminum in liquid iron using the relation expressed by Eq. (4). At all temperatures, the data determined at different nitrogen partial pressures of 0.2 and 0.97 atm show excellent linear relationships. The first-order interaction parameter, \( e_N^{Al} \), can be determined by a linear regression analysis of data in Fig. 5 as 0.017, 0.021 and 0.026 at 1873, 1923, and 1973 K, respectively. Using the Wagner’s reciprocal relationship, the value of \( e_N^{Al} \) can be also evaluated as 0.033, 0.040 and 0.050 at 1873, 1923, and 1973 K, respectively. The temperature dependence of \( e_N^{Al} \) value is shown in Fig. 6, and it can be expressed as 

\[
\frac{-332.2}{T} + 0.194
\]

where \( T \) is the temperature in K. Unfortunately, the original experimental data of Adachi et al.’s work are not available in the literature. However, it is interesting to see that the temperature dependence of \( e_N^{Al} \) values in the present study is opposite to Adachi et al.’s work. The validity of \( e_N^{Al} \) val-

Recently Ishii et al. measured the nitrogen solubility in iron melts containing aluminum up to 3.8 mass% at nitrogen partial pressures of 0.15–1.0 atm using the similar experimental technique as the present study. They reported the \( e_N^{Al} \) value as 0.017 in the temperature range of 1853–1953 K from the nitrogen solubility data in Fe–Al melts. In their work, the \( e_N^{Al} \) values determined by Adachi et al. are also tabulated as 0.025, 0.016 and 0.008 at 1873, 1923 and 1973 K, respectively. The experimental data of Adachi et al.’s work are not available in the literature. However, it is interesting to see that the temperature dependence of \( e_N^{Al} \) values in the present study is opposite to Adachi et al.’s work. The validity of \( e_N^{Al} \) val-

Fig. 4. Equilibrium relations between [%Al] and [%N] in Fe–Al–N melts at different N\(_2\) pressures and temperatures.

Fig. 5. Relations between log\( f_N^{Al} \) and [%Al] in Fe–Al–N melt.

Fig. 6. The \( e_N^{Al} \) values in Fe–Al–N melt.
ues determined in the present study will be discussed in the next section.

As mentioned earlier, the $e^{N}_{A1}$ values measured by some workers\textsuperscript{5,6} are negative. Evans and Pehlke\textsuperscript{5} used the Sieverts’ method to measure the equilibrium nitrogen solubility in liquid Fe–Al alloys containing up to 3.85 mass% Al in the temperature range of 1 873–2 023 K. They determined $e^{N}_{A1}$ as \(-0.028\) at 1 873 K, and they reported the temperature dependence of $e^{N}_{A1}$ values as \(828/T\). Later Wada and Pehlke\textsuperscript{6} used the same experimental method in the temperature range of 1 823–1 973 K, and reported the first-order interaction parameter, $r^{N}_{A1}$ and the second-order interaction parameter, $r^{N}_{AA}$ as \(-0.023\) and \(-0.016\), respectively at 1 873 K. In the earlier work by Pehlke and Elliot,\textsuperscript{2} however, they pointed out an inherent error of the Sieverts’ method caused by the vaporization and subsequent condensation of metal in the system. The metallic vapor may react with the nitrogen atmosphere to form a stable nitride or the nitrogen may be adsorbed on the finely divided deposit. This situation would increase the apparent absorption of nitrogen. These effects become significant for melts containing high concentrations of alloying elements which form stable nitrides or which have high vapor pressures.\textsuperscript{23} Aluminum is a stable nitride former and has a vapor pressure of about 50 times greater than liquid iron at 1 873 K.\textsuperscript{20}

3.2. Thermodynamics of AlN Formation in Liquid Iron

The solubility product of aluminum and nitrogen in liquid iron for AlN saturated condition was determined as shown as solid symbols in Fig. 4. Formation of pure AlN precipitates was confirmed by the SEM-EDS analysis as shown in Fig. 3. The reaction equilibrium for the formation of pure solid AlN in liquid iron can be written as

\[
\text{AlN(s)} = \text{Al} + \text{N} \quad \text{..................................(5)}
\]

\[
K_{\text{AlN}} = \frac{h_{\text{Al}}h_{\text{N}}}{a_{\text{AlN}}} = f_{\text{Al}}f_{\text{N}}[\%\text{Al}][\%\text{N}] \quad \text{..............(6)}
\]
where $K_{\text{AlN}}$ is the equilibrium constant for Reaction (5), and $h_{\text{Al}}$ and $h_{\text{N}}$ are the Henrian activities of aluminum and nitrogen relative to 1 mass% standard state in liquid iron, and $f_{\text{Al}}$ and $f_{\text{N}}$ are the activity coefficients of aluminum and nitrogen, respectively. Under the present experimental condition, the activity of aluminum nitride is unity.

The equilibrium constant, $K_{\text{AlN}}$, can be rewritten as the following relation using Wagner’s formalism:  

$$
\log K_{\text{AlN}}=\log f_{\text{Al}}+\log f_{\text{N}}+\log [\%\text{Al}][\%\text{N}]
$$

$$
=\epsilon_{\text{Al}}[\%\text{Al}]+\epsilon_{\text{N}}[\%\text{N}]
+\epsilon_{\text{Al}}[\%\text{N}]+\log [\%\text{Al}][\%\text{N}] \ldots \ldots \ldots \ldots \ldots \ldots (7)
$$

where $\epsilon_{\text{Al}}$ is the first-order self interaction parameter of aluminum in liquid iron, and the values of $\epsilon_{\text{Al}}$ and $\epsilon_{\text{N}}$ were obtained in the preceding section.

Figure 7 shows plots for the relation of Eq. (7) using the present experimental data of solubility product at 1873, 1923 and 1973 K. It is apparent from the figure that the data points determined at different nitrogen partial pressures and temperatures show excellent linear relationships. Therefore, the values of $\log K_{\text{AlN}}$ and $\epsilon_{\text{Al}}$ can be simultaneously obtained from the relations shown in Fig. 7. The values of $\log K_{\text{AlN}}$ obtained by extrapolating the lines are found to be $-1.434$, $-1.213$ and $-0.986$ at 1873, 1923 and 1973 K, respectively. The values of $\epsilon_{\text{Al}}$ can be obtained from the slope of lines as 0.043, 0.0415 and 0.04 at 1873, 1923 and 1973 K, respectively. The $\epsilon_{\text{Al}}$ values determined in the present study will be discussed more in detail in the next section.

The temperature dependence of $\log K_{\text{AlN}}$ values is shown in Fig. 8, and it can be expressed as $-16,560/T$ for the temperature range of 1873–1973 K. The standard free energy of decomposition of AlN in liquid iron is then given by Eq. (8).

$$
\Delta G^\circ_2=317100-141.7T \text{ J/mol} \ldots \ldots \ldots \ldots \ldots \ldots (8)
$$

The $\log K_{\text{AlN}}$ values determined by other workers are also shown in Fig. 8 and Table 4 for comparison. Evans et al. measured the solubility product of aluminum and nitrogen for AlN formation in liquid Fe–Al alloys by the Sieverts’ method in the temperature range of 1873–2023 K, by determining the break points in the Sieverts’ law lines of nitrogen solubility for the precipitation of AlN with increasing nitrogen partial pressure. They determined $\log K_{\text{AlN}}$ values from their experimental results and $\epsilon_{\text{Al}}$ value (=-828/T–0.471) using Eq. (7). In their calculation, however, they used the $\epsilon_{\text{Al}}$ value (=0.048 at 1873 K) reported by Wilder and Elliott. Wada et al. also used the Sieverts’ method to measure the solubility product of AlN in liquid iron in the temperature range of 1823–1973 K. They used the $\epsilon_{\text{Al}}$ value (=0.045 at 1873 K) reported by Woolley and Elliott to obtain $\log K_{\text{AlN}}$ value. Evans et al. and Wada et al. could not determine the $\epsilon_{\text{Al}}$ values from their own data due to the lack of experimental accuracy in determining the solubility product of AlN using the Sieverts’ method. Evans et al. carried out additional experiments to determine the solubility of aluminum and nitrogen in liquid iron contained in an AlN crucible at 1873 K under a fixed nitrogen partial pressure, and they pointed out that the metal–nitride–gas equilibration and sampling method would be a more reliable experimental technique for the nitride formation reaction equilibrium in liquid iron.

In the present study, the metal–nitride–gas equilibration technique utilizing a high frequency induction furnace provided an accurate measurement of the equilibrium solubility product for AlN formation in liquid iron. Therefore, the values of $\epsilon_{\text{Al}}$, $\epsilon_{\text{Al}}$ and $\log K_{\text{AlN}}$ could be determined together from the same experiment. Figure 9 compares the predictions of equilibrium solubility product of aluminum and nitrogen for AlN formation in liquid iron at 1903 K calculated from the interaction parameters and $\log K_{\text{AlN}}$ measured by different authors in Table 4 using Eq. (7). The experimental data for the solubility product of AlN at 1903 K measured by Wada et al. and Ishii et al. are also shown in the figure. As discussed earlier, the solubility product data measured by the Sieverts’ method show higher values than the data measured by the sampling method. The solubility product calculated from the thermodynamic data determined in the present study is in good agreement with Ishii et al.’s experimental data at 1903 K. The solubility product predicted using the recommended values in JSPS is not in good agreement with any of those experimental data. As mentioned earlier, the recommended values of $\epsilon_{\text{Al}}$, $\epsilon_{\text{Al}}$ and $\log K_{\text{AlN}}$ in JSPS were taken from the data of different investigations where the data were obtained by
completely different experimental techniques.

3.3. Thermodynamics of Al in Liquid Iron

Several investigators determined the activity of aluminum in liquid iron using various experimental techniques. Chipman and Floridis measured the distribution of aluminum between liquid iron and silver at 1873 K. They estimated the activity coefficient of aluminum in liquid iron at 1873 K. They reported the activity coefficient of aluminum in liquid iron as 0.043 and 0.053 at 1873 K, respectively.

Woolley and Elliott measured heats of solution in Fe–Al melts. They recommended the value of eAl in JSPS is expressed as 80.5/T, which has been derived by assuming the eAl value determined by Wilder et al. being inversely proportional to the absolute temperature as suggested by Rohde et al.

Darken developed a quadratic formalism for the representation of the excess integral and partial free energies in binary and ternary systems in the vicinity of a single component selected as the solvent. He showed that many liquid ferrous binary systems could be well represented by a quadratic formalism over a wide composition range.

\[
\ln \gamma_{\text{Al}} = \ln \gamma_{\text{Al}}^0 + e_{\text{Al}}^{\text{Al}} X_{\text{Al}} = -3.477 + 6.0X_{\text{Al}} \quad \text{(9)}
\]

where \(\gamma_{\text{Al}}^0 = 0.031\) at 1873 K, \(e_{\text{Al}}^{\text{Al}} = 6.0\) at 1873 K and \(X_{\text{Al}}\) are the first order self-interaction parameters in terms of mole fractions and the mole fraction of aluminum in Fe–Al melt, respectively. The value of \(e_{\text{Al}}^{\text{Al}}\) in Eq. (9) can be converted to the \(e_{\text{Al}}^{\text{Al}}\) value as 0.049 at 1873 K using the Lupis’ conversion relationship. Wilder and Elliott re-examined Chipman et al.’s data by measuring the activity of aluminum in Ag–Al alloys at higher temperatures up to 1253 K. They reported \(e_{\text{Al}}^{\text{Al}}\) and \(\gamma_{\text{Al}}^0\) values in liquid iron as 0.043 and 0.063 at 1873 K, respectively.

Woolley and Elliott measured heats of solution in Fe–Al melt up to 20.29 mass% Al at 1873 K using the high-temperature solution calorimeter technique. They reported values as 0.045 and 0.061 at 1873 K, respectively, by examining the data of Chipman et al. and Wilder et al. together with their molar heats of mixing in Fe–Al melts.

Belton and Fruehan directly measured the activity of aluminum in liquid Fe–Al alloys up to 14.49 mass% Al by Knudsen cell-mass spectrometry at 1873 K. They reported \(e_{\text{Al}}^{\text{Al}}\) and \(\gamma_{\text{Al}}^0\) values in liquid iron as 0.087 and 0.024 at 1873 K, respectively. Recently, Ichise et al. also used the same experimental technique to determine the activity of aluminum in liquid Fe–Al alloys up to 8.21 mass% Al in the temperature range of 1673–1873 K. They reported \(e_{\text{Al}}^{\text{Al}}\) and \(\gamma_{\text{Al}}^0\) values in liquid iron as 0.053 and 0.049 at 1873 K, respectively.

In the present study, the \(e_{\text{Al}}^{\text{Al}}\) value in Fe–Al–N melt up to 4.53 mass% Al was determined using the metal–nitride–gas equilibration technique as 0.043, 0.0415 and 0.040 at 1873, 1923 and 1973 K, respectively, as shown in Fig. 7. The temperature dependence of \(e_{\text{Al}}^{\text{Al}}\) is 111.0/T–0.016 as shown in Fig. 10 and Table 4 together with previously reported values. In spite of different experimental techniques, the values of \(e_{\text{Al}}^{\text{Al}}\) are quite well agreed in the range of 0.043–0.053 except for the data of Adachi et al. and Belton et al. The \(e_{\text{Al}}^{\text{Al}}\) value of 0.043 determined in the present study is the same as Wilder et al.’s data at 1873 K. The recommended value of \(e_{\text{Al}}^{\text{Al}}\) in JSPS is expressed as 80.5/T, which has been derived by assuming the \(e_{\text{Al}}^{\text{Al}}\) value determined by Wilder et al. being inversely proportional to the absolute temperature as suggested by Rohde et al.

As shown in Fig. 10, the change of \(e_{\text{Al}}^{\text{Al}}\) values with temperature determined in the present study is in excellent agreement with the recommended values in JSPS.

Darken developed a quadratic formalism for the representation of the excess integral and partial free energies in binary and ternary systems in the vicinity of a single component selected as the solvent. He showed that many liquid ferrous binary systems could be well represented by a quadratic formalism over a wide composition range.

\[
\log \gamma_1 = \alpha_{12} X_2^2 \quad \text{(10)}
\]

where the subscripts 1 and 2 are solvent and solute, respectively.

Darken also showed that in a ternary system if solute 2 or 3 has a very low concentration, the solution could be treated by the binary solution formalisms as shown in Eqs. (10) and (11). In the present study, the nitrogen content in Fe–Al–N melts saturated with AlN(s) is very low compared to the aluminum content. Therefore, if Darken’s quadratic formalism for Fe–Al melt is compared with the interaction parameter formalism for Fe–Al–N melt, the following relation is derived.

\[
\log \frac{\gamma_1}{\gamma_1^0} = \alpha_{\text{Fe–Al}} (\ -2X_1^2 + X_1^2) \\
= \frac{1}{2.303} (e_{\text{Al}}^{\text{Al}} X_1 + e_{\text{Al}}^{\text{N}} X_1) \quad \text{(12)}
\]
where \( e^{Al}_{N} \) term is negligible as compared to \( e^{Al}_{Al}X_{Al} \), and the values of \( e^{Al}_{Al} \) can be obtained from the \( e^{Al}_{Al} \) values determined in the present study using the Lupis’ conversion relationship\(^{19} \) as 5.3, 5.13 and 4.96 at 1 873, 1 923 and 1 973 K, respectively.

Figure 11 shows the relations of Eq. (12) using the solubility product data of aluminum and nitrogen for AlN formation in the present study. As shown in the figure, the remarkable linearity and zero intercept are illustrated within the composition range investigated in the present study. The values of \( a_{Fe–Al} \) from the slope of straight lines shown in Fig. 11 are \(-1.18, -1.16 \) and \(-1.15 \) at 1 873, 1 923 and 1 973 K, respectively. The \( a_{Fe–Al} \) values at 1 873 K determined by previous reports\(^{13–15} \) are also compared in the figure. The temperature dependence of \( a_{Fe–Al} \) values in the present study can be expressed as \(-1.112/T – 0.585 \).

According to Darken’s analysis\(^{15} \) on the Fe–Al system studied by Wilder et al.\(^{7} \), the \( a_{Fe–Al} \) value in Fe–Al system was determined as a constant value of \(-1.21 \) over the entire composition range at 1 873 K. This unique thermodynamic behavior of Fe–Al system allows us to calculate the \( \gamma_{Al}^o \) values simply by using Eq. (13).

\[
\log \gamma_{Al} = a_{Fe–Al}(1 – X_{Al})^2 \quad \text{.........(13)}
\]

Therefore, the \( \gamma_{Al}^o \) values as \( X_{Al} \rightarrow 0 \) can be obtained from the \( a_{Fe–Al} \) values as 0.066, 0.069 and 0.071 at 1 873, 1 923 and 1 973 K, respectively, in the present study. The temperature dependence of \( \gamma_{Al}^o \) is shown in Fig. 12 and Table 4, and compared with previous data. The \( \gamma_{Al}^o \) value of 0.066 at 1 873 K determined in the present study is in good agreement with the values of 0.063 and 0.061 reported by Wilder et al.\(^{7} \) and Woolley et al.\(^{12} \) respectively. However, the \( \gamma_{Al}^o \) values reported by Belton et al.\(^{13} \) and Ichise et al.\(^{14} \) using the Knudsen cell-mass spectrometry for Fe–Al melts differ significantly from those data determined by the chemical equilibration techniques.\(^{7,11,12} \)

4. Conclusions

The effect of aluminum on nitrogen solubility and the solubility product for AlN formation in liquid iron were determined using the metal–nitride–gas equilibration technique under various nitrogen partial pressures. The nitrogen solubility in liquid iron decreased with increasing aluminum content. Pure AlN was formed at critical aluminum and nitrogen contents in liquid iron. Using Wagner’s interaction parameter formalism, the first-order interaction parameter between aluminum and nitrogen, the first-order self interaction parameter of aluminum, and the equilibrium constant for the formation of pure solid AlN in liquid iron were determined in the temperature range of 1 873–1 973 K. Thermodynamics of aluminum in liquid iron determined in the present study could be well described by Darken’s quadratic formalism, and the values of \( a_{Fe–Al} \) and \( \gamma_{Al}^o \) in Fe–Al melt were determined as a function of temperature.

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